PAT-NO: JP408213644A

DOCUMENT-IDENTIFIER: JP 08213644 A

TITLE: PHOTOVOLTAIC ELEMENT

PUBN-DATE: August 20, 1996

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INT-CL (IPC): H01L031/04

ABSTRACT:

PURPOSE: To contrive to improve the photovoltaic conversion efficiency of a photovoltaic element by a method wherein at least one part of a doped layer, which is positioned on a light incident part, is provided with a polycrystalline semiconductor layer and the grains of a substance of a light refractive index smaller than that of the constituent substance of the polycrystalline semiconductor layer are contained in the polycrystalline semiconductor layer.

CONSTITUTION: A photovoltaic element is constituted of a P-type layer 3p, which consists of a P-type polycrystalline silicon

layer containing the grains of SiO<SB>2</SB> and is a doped layer which is positioned on a light incident side, and an N-type layer 3n, which become a main light generating layer and consists of an I-type amorphous silicon layer. The refractive index of the SiO<SB>2</SB> is smaller than that of polycrystalline silicon. As a result, when light enters the photovoltaic element, the light is scattered by the grains of the SiO<SB>2</SB> in the p-type polycrystalline silicon layer constituting the layer 3p, the angle of incidence of the light is changed and the light enters a solar cell layer 3. Accordingly, the optical path length of the light in the layer 3 can be increased without using a transparent electrode with the textured surface.

(19)日本国特許庁（JP）　(12) 公開特許公報(A)　(11)特許出願公開番号

特開平8－213644

(43)公開日　平成8年(1996)8月20日

(51)Int.Cl.6　識別記号　庁内整理番号　FI　技術表示箇所

H01L 31/04

H01L 31/04　A

B

F

審査請求　未請求　請求項の数4　OL　(全7頁)

(21)出願番号　特願平7－20337

(22)出願日　平成7年(1995)2月8日

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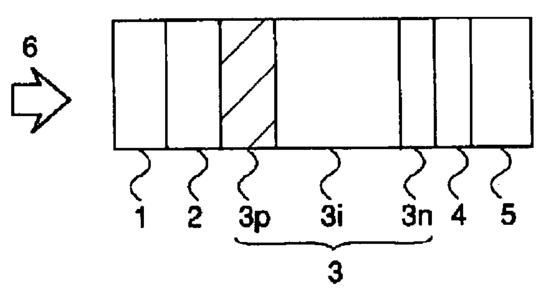
(54)【発明の名称】　光起電力素子

(57)【要約】

【目的】　光電変換効率の高い光起電力素子を提供する。

【構成】　光起電力素子を構成する太陽電池層の一部に、その構成物質よりも低屈折率の物質の粒を含む多結晶半導体層を備えているので、入射光を有効に散乱でき、光の光路長が延びることにより光電変換効率を向上できる。



【特許請求の範囲】

【請求項１】 光活性な半導体から成り、内部に半導体接合を少なくとも一つは有する光起電力素子に於いて、光入射側に位置するドープ層の少なくとも一部或いは主たる光発電層の光入射側の一部に多結晶半導体層を備え、該多結晶半導体層は、該層の構成物質よりも光屈折率の小さい物質の粒を含むことを特徴とする光起電力素子。

【請求項２】 光活性な半導体から成り、内部に半導体接合を少なくとも一つは有する光起電力素子に於いて、光透過側に位置するドープ層の少なくとも一部或いは主たる光発電層の光透過側の一部に多結晶半導体層を備え、該多結晶半導体層は、該層の構成物質よりも光屈折率の小さい物質の粒を含むことを特徴とする光起電力素子。

【請求項３】 光活性な半導体から成り、内部に半導体接合を少なくとも一つは有する光起電力素子に於いて、光入射側に位置するドープ層の少なくとも一部或いは主たる光発電層の光入射側の一部と、光透過側に位置するドープ層の少なくとも一部或いは主たる光発電層の光透過側の一部とに多結晶半導体層を備え、該多結晶半導体層は、該層の構成物質よりも光屈折率の小さい物質の粒を含んだことを特徴とする光起電力素子。

【請求項４】 前記光屈折率の小さい物質の粒の粒径が１０ｎｍ以上であることを特徴とする、請求項１、２及び３記載の光起電力素子。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、多結晶半導体層を含む光起電力素子に関するものである。

【０００２】

【従来の技術】太陽電池に代表される光起電力素子の光電変換効率向上のためには、入射光の有効利用が重要である。このために、特開昭６２－７７１６号に開示される如く、透明電極の表面を凸凹化、所謂テクスチャ化し、入射光をその表面で散乱させて主たる光発電層中での入射光の光路長を伸ばすことにより、入射光の有効利用を図った太陽電池が知られている。

【０００３】また、入射光の有効利用のための別の方法として、特開昭５５－１０８７８０号に開示される如く、裏面電極とドープ層との界面に透明導電層を備えたことで、ドープ層側から透過して裏面電極に達した光の反射率を増大させた太陽電池が知られている。

【０００４】図8は、従来の太陽電池の構造図である。同図に於いて、1はガラス基板、2は表面がテクスチャ化された透明電極である。3は太陽電池層であり、ｐ型非晶質シリコンカーバイドから成るｐ層３ｐ、主たる光発電層となるｉ型非晶質シリコンから成るｉ層３ｉ及びｎ型非晶質シリコンから成るｎ層３ｎから成る。また4は透明導電層であり、5はＡｇ，Ａｌ等の金属から成る

裏面電極である。

【０００５】同図の左側から入射した光6は、透明電極2のテクスチャ化された表面で散乱され太陽電池層3に入る。この時太陽電池層３中に斜めに入る光の割合が増加しているので、該層３中での光路長が増大することにより光の吸収量が増え、このため入射光の有効利用が図れる。

【０００６】また、太陽電池層3に吸収されずに裏面側に透過した光は、裏面電極5に反射され再び太陽電池層3に入射する。この時光透過側のドープ層であるｎ層３ｎと裏面電極5との界面に透明導電層4が備えられているので、該界面においてｎ層３ｎを構成するｎ型非晶質シリコンと裏面電極5を構成する金属との合金化が生じない。このために裏面電極5は高い反射率を保持することができるので、太陽電池層3に再び入射する光の量が増し、光の有効利用を図れる。

【０００７】

【発明が解決しようとする課題】然し乍ら、上記の透明電極を用いると、表面がテクスチャ化されているために太陽電池層内で電界の不均一が生じ、太陽電池特性の一つである曲線因子（Ｆ．Ｆ．）が低下するという問題があった。

【０００８】また、ドープ層と裏面電極との界面に透明導電層を設けた太陽電池では、該界面に於ける合金化の問題は解決できるものの、裏面電極で反射された光には散乱成分が少ないために反射光の太陽電池層中での光路長は短く、この点に改善の余地が残されていた。

【０００９】本発明は、従来の上記の問題を解決し、入射光を有効に利用することにより、光電変換効率の高い光起電力素子を提供することを目的とする。

【００１０】

【課題を解決するための手段】本発明の光起電力素子は、光活性な半導体から成り、内部に半導体接合を少なくとも一つは有する光起電力素子に於いて、光入射側に位置するドープ層の少なくとも一部或いは主たる光発電層の光入射側の一部に多結晶半導体層を備え、該多結晶半導体層は、該層の構成物質よりも光屈折率の小さい物質の粒を含んだことを特徴とする。

【００１１】また、光活性な半導体から成り、内部に半導体接合を少なくとも一つは有する光起電力素子に於いて、光透過側に位置するドープ層の少なくとも一部或いは主たる光発電層の光透過側の一部に多結晶半導体層を備え、該多結晶半導体層は、該層の構成物質よりも光屈折率の小さい物質の粒を含んだことを特徴とする。

【００１２】もしくは、光活性な半導体から成り、内部に半導体接合を少なくとも一つは有する光起電力素子に於いて、光入射側に位置するドープ層の少なくとも一部或いは主たる光発電層の光入射側の一部と、光透過側に位置するドープ層の少なくとも一部或いは主たる光発電層の光透過側の一部とに多結晶半導体層を備え、該多結

晶半導体層は、該層の構成物質よりも光屈折率の小さい物質の粒を含んだことを特徴とする。

【0013】前記光屈折率の小さい物質としては、シリコン酸化物，シリコン窒化物，酸化鉛，酸化錫，ＣｄＳ，ＺｎＰ、或いはこれらの混合物を用いることができる。

【0014】また、前記光屈折率の小さい物質の粒の粒径が１０ｎｍ以上、好ましくは３０ｎｍ以上であることを特徴とする。

【0015】

【作用】本発明の光起電力素子は、光活性な半導体から成り、内部に半導体接合を少なくとも一つは有する光起電力素子であり、光入射側に位置するドープ層の少なくとも一部に多結晶半導体層を備え、該多結晶半導体層は、該層の構成物質よりも光屈折率の小さい物質の粒を含んでいる。もしくは、前記多結晶半導体層を、主たる光発電層の光入射側の一部に備えている。このために、入射光は多結晶半導体層中の光屈折率の小さい物質の粒により散乱され、表面をテクスチャ化した透明電極を用いなくとも太陽電池層中での光路長を増大できる。従って、Ｆ．Ｆ．の低下を生じさせることなく入射光の有効利用が図れる。

【0016】また、本発明の光起電力素子は、上記の多結晶半導体層を、光透過側に位置するドープ層の少なくとも一部、或いは主たる光発電層の光透過側の一部に備えている。このために、半導体層を通過してきた光は多結晶半導体層中の光屈折率の小さい物質の粒により散乱され、角度を変えて裏面電極に到達する。従って、裏面電極での反射光の散乱成分が増加し、光路長が増大するため入射光の有効利用が図れる。

【0017】もしくは、本発明の光起電力素子は、上記の多結晶半導体層を、光入射側に位置するドープ層の少なくとも一部或いは主たる光発電層の光入射側の一部と、光透過側に位置するドープ層の少なくとも一部或いは主たる光発電層の光透過側の一部とに備えている。こ

のために、上記の二つの効果を組み合わせた光起電力素子を提供でき、光電変換効率の高い光起電力素子を提供できる。

【0018】前記光屈折率の小さい物質としては、シリコン酸化物，シリコン窒化物，酸化鉛，酸化錫，ＣｄＳ，ＺｎＰ、或いはこれらの混合物を用いることができる。

【0019】加えて光屈折率の小さい物質の粒の粒径が１０ｎｍ以上、さらに好ましくは３０ｎｍ以上であるので、入射光を効果的に散乱できる。

【0020】

【実施例】図１は、本発明の光起電力素子の実施例を示す構造図である。同図に於いて、１はガラス基板、２はSnO_2から成る膜厚６０００Åの透明電極であり、表面はテクスチャ化していない。３は太陽電池層であり、SiO_2の粒を内部に含むｐ型多結晶シリコンから成る膜厚１０００Åのｐ層３ｐ、主たる光発電層となるｉ型非晶質シリコンから成る膜厚４０００Åのｉ層３ｉ、及びｎ型非晶質シリコンから成る膜厚１００Åのｎ層３ｎから構成される。また４はＩＴＯから成る透明導電層であり、５はＡｇから成る裏面電極である。

【0021】透明電極２は熱ＣＶＤ法を用いて形成し、ｉ層３ｉ及びｎ層３ｎは、プラズマＣＶＤ法を用いて形成した。また透明導電層４及び裏面電極５はスパッタ法で形成した。

【0022】本実施例の光起電力素子では、光入射側のドープ層であるｐ層３を、SiO_2粒を内部に含むｐ型多結晶シリコンで構成している。このｐ層３ｐは、まずプラズマＣＶＤ法を用いて酸素を含むｐ型非晶質シリコンを形成した後に、レーザアニールを施して結晶化させ、形成した。ｐ型非晶質シリコンの形成条件及びレーザアニール条件を表１及び表２に示す。

【0023】

【表１】

原料ガス	SiH_4：50sccm CO_2：10sccm B_2H_6：0.5sccm H_2：100sccm
基板温度	200℃
RFパワー	20mW／cm^2
反応圧力	27Pa

【0024】
【表2】

レーザ種類	ArFエキシマレーザ
レーザ波長	193nm
レーザパワー	200mJ／パルス
パルス長	5nsec
パルス数	10パルス
温度	100℃

【0025】この様に、酸素を含むp型非晶質シリコンを形成した後にレーザアニールを施すと、非晶質シリコンは結晶化して多結晶シリコンとなる。この時非晶質シリコン中に含まれていた酸素は、SiO_2もしくはこれに近い組成のシリコン酸化物として多結晶シリコン中にランダムに分散して偏析し、粒状になる。以上の工程で、SiO_2の粒を内部に含むp型多結晶シリコンが形成される。尚SiO_2の粒の粒径は、非晶質シリコンの形成条件、或いはレーザアニールの条件を変えることで制御できる。

【0026】本実施例に於いては、SiO_2の屈折率が約1.5と多結晶シリコンの屈折率（約3.4）よりも小さいために、本実施例の光起電力素子に光が入射すると、光はp層3pを構成するp型多結晶シリコン中のSiO_2の粒により散乱され、入射角度を変えて太陽電池＊層3に入射する。従って、本実施例の光起電力素子は、表面をテクスチャ化した透明電極を用いずに、太陽電池層3中での光の光路長を増大できる。このため表面をテクスチャ化した透明電極を用いたときに問題となっていた、電界の不均一によるF．F．の低下を生じさせることなく出力電流を増大できるので、光電変換効率を向上できる。

【0027】表3に、SiO_2粒の粒径を変化させた本実施例の光起電力素子の光電変換効率を示す。尚、比較例として表面をテクスチャ化しない透明電極を用いた構造の光起電力素子を形成したが、この光起電力素子の光電変換効率は9．5％であった。

【0028】
【表3】

粒径（nm）	光電変換効率（%）
5	9.5
10	10.5
20	10.7
30	10.8
50	10.9
100	10.8

【0029】表3からわかるように、本実施例の光起電力素子の光電変換効率は、SiO_2粒の粒径が5nmの場合には光の散乱が充分ではなく、9．5%と比較例の光起電力素子と同じであった。しかし、粒径が大きくなるに連れ光電変換効率は向上し、粒径が10nmになると10．5%と、図8に示した従来構造の光起電力素子と同程度の光電変換効率が得られ、特に30nm以上ではほぼ11%の高い光電変換効率が得られた。

【0030】さらに、本実施例に於いて、透明電極2を表面のテクスチャ化の度合いが小さいSnO_2で構成すると、F．F．の低下も少なくまた入射光の散乱の効果を一層高めることができるので、光電変換効率のより一層の向上が図れる。

【0031】尚、本実施例では光入射側のドープ層であるp層3pの全体をSiO_2の粒を内部に含むp型多結晶シリコンで構成したが、上記の説明から明らかなように、p層の一部をSiO_2の粒を内部に含むp型多結晶シリコンで構成しても良い。或いは主たる光発電層であるi層の光入射側の一部に、SiO_2の粒を内部に含むi型多結晶シリコン層を設けても同じ効果が得られる。図2及び図3はこの例を示し、図2はSiO_2の粒を内部に含むp型多結晶シリコン層31pをp層3pの一部に設けた光起電力素子の構造図、また図3はSiO_2の粒を内部に含むi型多結晶シリコン層31iをi層3iの光入射側の一部に設けた光起電力素子の構造図である。尚、図2に於いて32pはp型の非晶質シリコン層であり、図3に於いて、32i及び33iはi型の非晶質シリコン層である。図3（b）に示すように、i層3iの光入射側の一部にSiO_2の粒を内部に含むi型多結晶シリコン層を設ける場合、該層をp層3pと接して設ける必要はない。

【0032】図4は、本発明の光起電力素子の他の実施例を示す構造図である。同図に於いて、1はガラス基板、2は膜厚6000Åの、表面がテクスチャ化されたSnO_2から成る透明電極である。3は太陽電池層であり、p型非晶質シリコンカーバイドから成る膜厚100Åのp層3p、主たる光発電層であるi型非晶質シリコンから成る膜厚3000Åのi層3i、及び光透過側のドープ層である、SiO_2の粒を内部に含むn型多結晶シリコンから成る膜厚1000Åのn層3nから構成される。4はITOから成る透明導電層であり、5はAgから成る裏面電極である。

【0033】これらの形成法は前述の実施例と同じである。SiO_2の粒を内部に含むn型多結晶シリコンから成るn層3nは、プラズマCVD法を用いて酸素を含むn型非晶質シリコンを形成した後に、レーザアニールを施すことで結晶化させて形成した。

【0034】本実施例の光起電力素子に光が入射すると、i層3に吸収されず、該層を透過した光はn層3nを構成するn型多結晶シリコン中のSiO_2粒により散乱される。散乱された光は角度を変えて裏面電極5に到達するために、裏面電極5で反射されて再度太陽電池層3に入射する光も散乱成分が多くなる。このために太陽電池層3内での光の光路長が増大し光の有効利用が図れ、出力電流が増大することにより、光電変換効率が向上する。

【0035】表4に、SiO_2粒の粒径を変化させて形成した本実施例の光起電力素子の光電変換効率を示す。尚、図8に示した従来構造の光起電力素子の光電変換効率は10．5%であった。

【0036】

【表4】

粒径（nm）	光電変換効率（％）
5	10．5
10	10．6
20	10．9
30	11．1
50	11．3
100	11．2

【0037】表4からわかるように、本実施例の光起電力素子の光電変換効率は、SiO_2粒の粒径が5nmの場合には光の散乱が充分ではなく、10．5％と従来構造の光起電力素子と同じであった。しかし、粒径が大きくなるに連れ光電変換効率は向上し、粒径が10nmでは10．6％と従来よりも高い光電変換効率が得られ、特に30nm以上では11％以上の高い光電変換効率が得られた。

【0038】また、本実施例では光透過側のドープ層であるn層3nの全体を、SiO_2の粒を内部に含むn型多結晶シリコンで構成したが、前述の実施例と同様に、n層の一部をSiO_2の粒を内部に含むn型多結晶シリコンで構成しても良いし、i層の光透過側の一部にSiO_2の粒を内部に含むi型多結晶シリコン層を設けても同じ効果が得られる。図5にこれらの一例を示す。同図は、n層3nの光透過側の一部にSiO_2の粒を内部に含むn型多結晶シリコン層32nを設けた光起電力素子の構造図である。

【0039】図6は、本発明の光起電力素子のさらに別の構造図である。同図（a）ではp層3p及びn層3nを、それぞれがSiO_2の粒を内部に含むp型多結晶シリコン及びn型多結晶シリコンで構成している。また、同図（b）は、p層3p及びi層の光透過側の一部31iを、それぞれがSiO_2の粒を内部に含むp型多結晶シリコン及びi型多結晶シリコンで構成した光起電力素子の構造図である。これらの構造にすることで、光入射側及び裏面側での光の散乱効果を同時に達成することができるので、入射光のより一層の有効利用が図れる。尚、図6（b）の構造の代わりに、i層の光入射側の一部及びn層を、それぞれがSiO_2の粒を内部に含むi型多結晶シリコン及びn型多結晶シリコンで構成しても同様の効果が得られることは言うまでもない。

【0040】以上の実施例では主たる光発電層の材料として非晶質シリコンを用いたが、これに限るものでなく、例えばa－SiGe：H、結晶シリコン、多結晶シリコン等を主たる光発電層とした光起電力素子にも適用できる。

【0041】図7は、主たる光発電層として多結晶シリコンを用いた光起電力素子の構造図である。同図に於いて、7はステンレス基板、8は主たる発電層となる膜厚2μmのSiO_2粒を内部に含むn型多結晶シリコン層である。9は膜厚50Åのi型非晶質シリコンから成るバッファ層、10は膜厚200Åのp型非晶質シリコンから成るp層、10は膜厚1000ÅのITOから成る透明電極、11はAgから成る集電極である。

【0042】SiO_2を内部に含む多結晶シリコン層8は、プラズマCVD法を用いて表1と同じ条件で酸素を含むn型非晶質シリコンを形成した後に、真空中で10時間800℃の温度で熱アニールを施すことにより固相成長させて形成した。固相成長の場合も、前述したレーザアニールの場合と同様に、非晶質シリコンは多結晶シリコンとなるが、その際に非晶質シリコン中に含まれる酸素はSiO_2或いはこれに近い組成で多結晶シリコン中にランダムに分散して偏析し、粒状となる。

【0043】本実施例の場合にも、入射光はn型多結晶シリコン8中のSiO_2粒により散乱され、光の光路長が増大することにより出力電流が向上する。

【0044】尚、光屈折率の小さい物質としては以上の実施例で述べてきたSiO_2以外に、シリコン窒化物、酸化鉛、酸化錫、CdS、ZnP或いはこれらの混合物を用いることができる。

【0045】

【発明の効果】本発明の光起電力素子は、光屈折率の小さい物質の粒を含んだ多結晶半導体層を、光起電力素子層の一部に備えている。入射光は多結晶半導体層中の光屈折率の小さい物質の粒により散乱される。このため、該層を設けた位置に応じて、光起電力素子層中での光路長が増大する、或いは裏面での反射光の散乱成分が増える、もしくはこの両方の効果が発生し、入射光の有効利用が図れる。

【0046】前記光屈折率の小さい物質としてはシリコン酸化物，シリコン窒化物，酸化鉛，酸化錫，CdS，ZnP、或いはこれらの組み合わせを用いていることができる。

【0047】また、光屈折率の小さい物質の粒の粒径を10nm以上、好ましくは30nm以上としているので、入射光を効果的に散乱できる。

【図面の簡単な説明】

【図1】　本発明の光起電力素子の実施例を説明する構造図である。

【図2】　SiO_2の粒を内部に含むp型多結晶シリコ

ン層をｐ層の一部に設けた光起電力素子の構造図である。

【図3】 ＳｉＯ$_2$の粒を内部に含むｉ型多結晶シリコン層をｉ層の光入射側の一部に設けた光起電力素子の構造図である。

【図4】 ＳｉＯ$_2$の粒を内部に含むｎ型多結晶シリコン層をｎ層に設けた光起電力素子の構造図である。

【図5】 ＳｉＯ$_2$の粒を内部に含むｎ型多結晶シリコン層をｎ層の一部に設けた光起電力素子の構造図である。

【図6】 それぞれがＳｉＯ$_2$の粒を内部に含む多結晶シリコン層を、ｐ層及びｎ層、或いはｐ層及びｉ層の光透過側の一部に設けた光起電力素子の構造図である。

【図7】 主たる光発電層として多結晶シリコンを用いた本発明の光起電力素子の実施例を示す構造図である。

【図8】 従来の光起電力素子の構造図である。

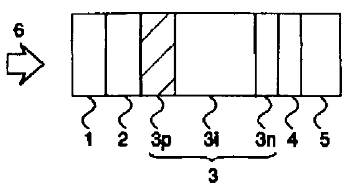
【符号の説明】

１・・ガラス基板、２・・透明電極、３・・太陽電池層、３ｐ・・ｐ層、３ｉ・・ｉ層、３ｎ・・ｎ層、４・・透明導電層、５・・裏面電極、６・・入射光、７・・ステンレス基板

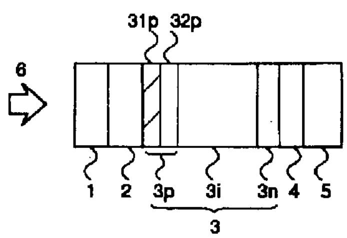
８・・ＳｉＯ$_2$を内部に含む多結晶シリコン層、９・・バッファ層、１０・・透明電極

１１・・集電極、３１ｐ・・ＳｉＯ$_2$の粒を内部に含むｐ型多結晶シリコン層、３１ｉ・・ＳｉＯ$_2$の粒を内部に含むｉ型多結晶シリコン層、３２ｎ・・ＳｉＯ$_2$の粒を内部に含むｎ型多結晶シリコン層

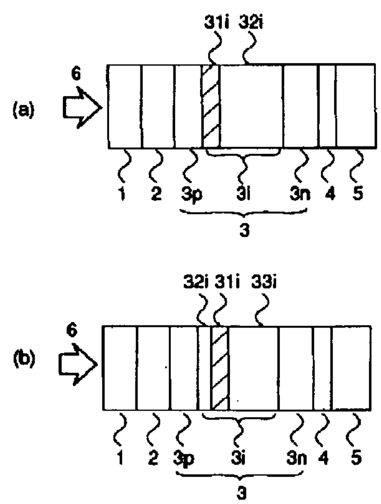
【図1】



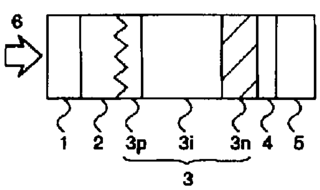
【図2】



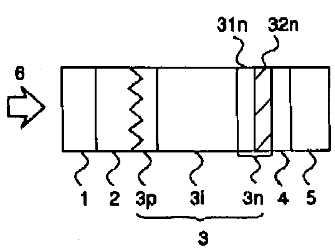
【図3】



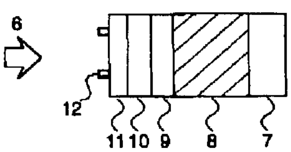
【図4】



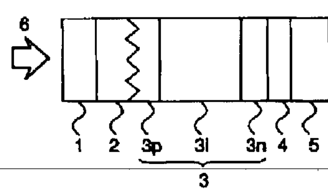
【図5】



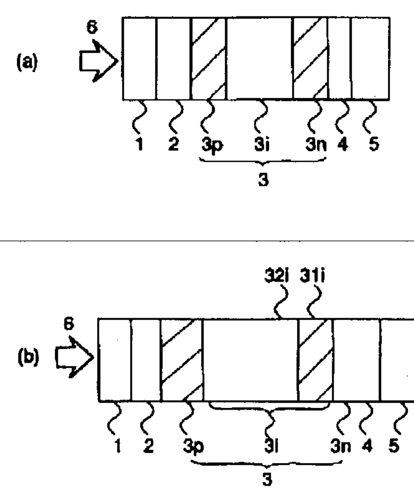
【図7】



【図8】



【図6】



CLAIMS

[Claim(s)]
[Claim 1] light -- the photovoltaic cell characterized by consisting of an activity semi-conductor, equipping with a polycrystal semi-conductor layer a part of dope layer [at least] located in the interior at an optical incidence side in the photovoltaic cell in which at least one has semi-conductor junction, or the part by the side of the optical incidence of a main optical generation-of-electrical-energy layer, and this polycrystal semi-conductor layer containing the grain of the matter with an optical refractive index smaller than the constituent of this layer.
[Claim 2] light -- the photovoltaic cell characterized by consisting of an activity semi-conductor, equipping with a polycrystal semi-conductor layer a part of dope layer [at least] located in the interior at a light transmission side in the photovoltaic cell in which at least one has semi-conductor junction, or the part by the side of the light transmission of a main optical generation-of-electrical-energy layer, and this polycrystal semi-conductor layer containing the grain of the matter with an optical refractive index smaller than the constituent of this layer.
[Claim 3] light -- consisting of an activity semi-conductor, at least one semi-conductor junction in the photovoltaic cell which it has with a part of dope layer [at least] in which it is located at an optical incidence side, or the part by the side of the optical incidence of a main optical generation-of-electrical-energy layer inside It is the photovoltaic cell which equips with a polycrystal semi-conductor layer a part of dope layer [at least] located in a light transmission side, or the part by the side of the light transmission of a main optical generation-of-electrical-energy layer, and is characterized by this polycrystal semi-conductor layer containing the grain of the matter with an optical refractive index smaller than the constituent of this layer.
[Claim 4] The photovoltaic cell of claims 1 and 2 and 3 publications which are characterized by the particle size of the grain of the matter with said optical small refractive index being 10nm or more.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the photovoltaic cell containing a polycrystal semi-conductor layer.
[0002]
[Description of the Prior Art] For the improvement in photoelectric conversion efficiency of the photovoltaic cell represented by the solar battery, a deployment of incident light is important. For this reason, the solar battery aiming at a deployment of incident light is known in the front face of a transparent electrode uneven-izing and by [so-called] texture-izing, scattering incident light on that front face, and lengthening the optical path length of the incident light in the inside of a main optical generation-of-electrical-energy layer so that it may be indicated by JP,62-7716,A.
[0003] Moreover, as an option for a deployment of incident light, the solar battery which increased the reflection factor of light which penetrated from the dope layer side and reached the rear-face electrode by having equipped the interface of a rear-face electrode and a dope layer with the transparence conductive layer is known so that it may be indicated by JP,55-108780,A.
[0004] Drawing 8 is structural drawing of the conventional solar battery. In this drawing, it is the transparent electrode with which, as for 1, were-izing [the glass substrate] and, as for 2, the front face was texture-ized. 3 is a solar-battery layer and consists of n-layer 3n which consists of i layer 3i and n mold amorphous silicon which consist of i mold amorphous silicon used as p which consist of p mold amorphous silicon carbide layer 3p, and a main optical generation-of-electrical-energy layer. Moreover, 4 is a transparence conductive layer and 5 is a rear-face electrode which consists of metals, such as Ag and aluminum.
[0005] The light 6 which carried out incidence from the left-hand side of this drawing is scattered about on the front face on which the transparent electrode 2 was texture-ized, and goes into the solar-battery layer 3. Since the rate of the light which enters aslant into the solar-battery layer 3 at this time is increasing, when the optical path length in the inside of this layer 3 increases, the amount of absorption of light increases and, for this reason, a deployment of incident light can be aimed at.
[0006] Moreover, it is reflected by the rear-face electrode 5 and incidence of the light penetrated to the rear-face side, without being absorbed by the solar-battery layer 3 is again carried out to the solar-battery layer 3. Since the interface of the n layer 3n and the rear-face electrode 5 which are a dope layer by the side of this Tokimitsu transparency is equipped with the transparence conductive layer 4, alloying with n mold amorphous silicon which constitutes n-layer 3n in this interface, and the metal which constitutes the rear-face electrode 5 does not arise. For this reason, since the rear-face electrode 5 can hold a high reflection factor, the amount of the light which carries out incidence to the solar-battery layer 3 again can aim at a deployment of increase and light.
[0007]
[Problem(s) to be Solved by the Invention] However, when ** et al. and the above-mentioned transparent electrode were used, since the front face was texture-ized, the ununiformity of electric field arose within the solar-battery layer, and there was a problem that the curvilinear factor (F. F.) which is one of the solar-battery properties fell.
[0008] Moreover, in the solar battery which prepared the transparence conductive layer in the interface of a dope layer and a rear-face electrode, although the problem of the alloying in this interface was solvable, since the light reflected with the rear-face electrode had few dispersion components, the optical path length in the inside of the solar-battery layer of the reflected light was short, and the room of an improvement was left behind to this point.
[0009] This invention aims at offering a photovoltaic cell with high photoelectric conversion efficiency by solving the conventional above-mentioned problem and using incident light effectively.
[0010]
[Means for Solving the Problem] the photovoltaic cell of this invention -- light -- it consists of an activity semi-

conductor, a part of dope layer [at least] located in the interior at an optical incidence side in the photovoltaic cell in which at least one has semi-conductor junction, or the part by the side of the optical incidence of a main optical generation-of-electrical-energy layer is equipped with a polycrystal semi-conductor layer, and this polycrystal semi-conductor layer is characterized by including the grain of the matter with an optical refractive index smaller than the constituent of this layer.

[0011] moreover, light -- it consists of an activity semi-conductor, a part of dope layer [at least] located in the interior at a light transmission side in the photovoltaic cell in which at least one has semi-conductor junction, or the part by the side of the light transmission of a main optical generation-of-electrical-energy layer is equipped with a polycrystal semi-conductor layer, and this polycrystal semi-conductor layer is characterized by including the grain of the matter with an optical refractive index smaller than the constituent of this layer.

[0012] or light -- consisting of an activity semi-conductor, at least one semi-conductor junction in the photovoltaic cell which it has with a part of dope layer [at least] in which it is located at an optical incidence side, or the part by the side of the optical incidence of a main optical generation-of-electrical-energy layer inside A part of dope layer [at least] located in a light transmission side or the part by the side of the light transmission of a main optical generation-of-electrical-energy layer is equipped with a polycrystal semi-conductor layer, and this polycrystal semi-conductor layer is characterized by including the grain of the matter with an optical refractive index smaller than the constituent of this layer.

[0013] As matter with said optical small refractive index, a silicon oxide, a silicon nitride, lead oxide, tin oxide, CdS(s) and ZnP(s), or such mixture can be used.

[0014] Moreover, particle size of the grain of the matter with said optical small refractive index is characterized by being [10nm or more] 30nm or more preferably.

[0015]

[Function] the photovoltaic cell of this invention -- light -- it consists of an activity semi-conductor, and it is the photovoltaic cell to which at least one has semi-conductor junction inside, a part of dope layer [at least] located in an optical incidence side is equipped with a polycrystal semi-conductor layer, and this polycrystal semi-conductor layer contains the grain of the matter with an optical refractive index smaller than the constituent of this layer. Or the part by the side of the optical incidence of a main optical generation-of-electrical-energy layer is equipped with said polycrystal semi-conductor layer. For this reason, incident light is scattered about with the grain of the matter with the optical small refractive index in a polycrystal semi-conductor layer, and even if it does not use the transparent electrode which texture-ized the front face, it can increase the optical path length in the inside of a solar-battery layer. Therefore, a deployment of incident light can be aimed at, without producing lowering of F.F.

[0016] Moreover, at least, or the photovoltaic cell of this invention equips the part by the side of the light transmission of a main optical generation-of-electrical-energy layer with the above-mentioned polycrystal semi-conductor layer. [the dope layer located in a light transmission side] For this reason, the light which has passed the semi-conductor layer is scattered about with the grain of the matter with the optical small refractive index in a polycrystal semi-conductor layer, changes an include angle, and reaches a rear-face electrode. Therefore, the dispersion component of the reflected light in a rear-face electrode increases, and since the optical path length increases, a deployment of incident light can be aimed at.

[0017] Or the photovoltaic cell of this invention equips with the above-mentioned polycrystal semi-conductor layer a part of dope layer [at least] located in an optical incidence side or the part by the side of the optical incidence of a main optical generation-of-electrical-energy layer, a part of dope layer [at least] located in a light transmission side, or the part by the side of the light transmission of a main optical generation-of-electrical-energy layer. For this reason, the photovoltaic cell which combined the two above-mentioned effectiveness can be offered, and a photovoltaic cell with high photoelectric conversion efficiency can be offered.

[0018] As matter with said optical small refractive index, a silicon oxide, a silicon nitride, lead oxide, tin oxide, CdS(s) and ZnP(s), or such mixture can be used.

[0019] In addition, 10nm or more, since the particle size of the grain of the matter with an optical small refractive index is 30nm or more still more preferably, they can be effectively scattered about in incident light.

[0020]

[Example] Drawing 1 is structural drawing showing the example of the photovoltaic cell of this invention. In this drawing, 1 is a glass substrate and a transparent electrode of 6000A of thickness with which 2 consists of SnO_2, and the front face is not texture-ized. 3 is a solar-battery layer and consists of n-layer 3n of 100A of thickness which consists of i layer 3i and n mold amorphous silicon of 4000A of thickness which consists of i mold amorphous silicon used as p layer 3p and a main optical generation-of-electrical-energy layer of 1000A of thickness which consists of p mold polycrystalline silicon which contains the grain of SiO_2 inside. Moreover, 4 is a transparence conductive layer which

·consists of ITO, and 5 is a rear-face electrode which consists of Ag.
[0021] The transparent electrode 2 was formed using the heat CVD method, and was formed n-layer i layer 3i and 3n using the plasma-CVD method. Moreover, the transparence conductive layer 4 and the rear-face electrode 5 were formed by the spatter.
[0022] p mold polycrystalline silicon which is a dope layer by the side of optical incidence and which contains two grains of SiO(s) inside constitutes 3 [p-layer] from the photovoltaic cell of this example. After forming p mold amorphous silicon which contains oxygen using a plasma-CVD method first, this p layer 3p gives laser annealing, made it crystallize, and was formed. The formation conditions and laser annealing conditions of p mold amorphous silicon are shown in a table 1 and a table 2.
[0023]
[A table 1]

原料ガス	SiH_4 ：50sccm CO_2 ：10sccm B_2H_6 ：0．5sccm H_2 ：100sccm
基板温度	200℃
RFパワー	20mW／cm^2
反応圧力	27Pa

[0024]
[A table 2]

レーザ種類	ArFエキシマレーザ
レーザ波長	193nm
レーザパワー	200mJ／パルス
パルス長	5nsec
パルス数	10パルス
温度	100℃

[0025] Thus, if laser annealing is given after forming p mold amorphous silicon containing oxygen, it will crystallize and amorphous silicon will turn into polycrystalline silicon. As a silicon oxide of the presentation near SiO2 or this, it distributes at random, and the oxygen contained in amorphous silicon at this time is segregated in polycrystalline silicon, and becomes grain-like. At the above process, p mold polycrystalline silicon which contains the grain of SiO2 inside is formed. In addition, the particle size of the grain of SiO2 is controllable by changing the formation conditions of amorphous silicon, or the conditions of laser annealing.

[0026] In this example, since the refractive index of SiO2 is smaller than the refractive index (about 3.4) of about 1.5 and polycrystalline silicon, if light carries out incidence to the photovoltaic cell of this example, light will be scattered about with the grain of SiO2 in p mold polycrystalline silicon which constitutes p layer 3p, will change whenever [incident angle], and it will carry out incidence to the solar-battery layer 3. Therefore, the photovoltaic cell of this example can increase the optical path length of the light in the inside of the solar-battery layer 3, without using the transparent electrode which texture-ized the front face. For this reason, since the output current can be increased without producing lowering of F.F. by the ununiformity of electric field used as a problem when the transparent electrode which texture-ized the front face is used, photoelectric conversion efficiency can be improved.
[0027] The photoelectric conversion efficiency of the photovoltaic cell of this example to which the particle size of two grains of SiO(s) was changed is shown in a table 3. In addition, although the photovoltaic cell of structure using the transparent electrode which does not texture-ize a front face as an example of a comparison was formed, the photoelectric conversion efficiency of this photovoltaic cell was 9.5%.
[0028]
[A table 3]

粒径（ｎｍ）	光電変換効率（％）
５	９．５
１０	１０．５
２０	１０．７
３０	１０．８
５０	１０．９
１００	１０．８

[0029] As shown in a table 3, when the particle size of two grains of SiO(s) was 5nm, the photoelectric conversion efficiency of the photovoltaic cell of this example did not have enough dispersion of light, and it was the same as that of 9.5% and the photovoltaic cell of the example of a comparison. [of it] However, photoelectric conversion efficiency improved, particle size took for becoming large, when particle size was set to 10nm, the photoelectric conversion efficiency comparable as the photovoltaic cell of structure indicated to be 10.5% to drawing 8 was acquired conventionally, and by 30nm or more, about 11% of high photoelectric conversion efficiency was especially acquired.
[0030] Furthermore, in this example, if the degree of surface texture-izing constitutes a transparent electrode 2 from small SnO2, since lowering of F.F. can also heighten the effectiveness of dispersion of incident light further few again, much more improvement in photoelectric conversion efficiency can be aimed at.
[0031] In addition, although p mold polycrystalline silicon which contains the grain of SiO2 inside constituted the whole p layer 3p which is a dope layer by the side of optical incidence from this example, a part of p layers may consist of p mold polycrystalline silicon which contains the grain of SiO2 inside so that clearly from the above-mentioned explanation. Or the same effectiveness is acquired even if it prepares i mold polycrystalline silicon layer which contains the grain of SiO2 inside in the part by the side of the optical incidence of i layers which is a main optical generation-of-electrical-energy layer. Structural drawing of the photovoltaic cell which prepared p mold polycrystalline silicon layer 31p in which drawing 2 and drawing 3 show this example to, and drawing 2 contains the grain of SiO2 inside in a part of p layer 3p, and drawing 3 are structural drawings of the photovoltaic cell which prepared i mold polycrystalline silicon layer 31i which contains the grain of SiO2 inside in the part by the side of the optical incidence of i layer 3i. In addition, in drawing 2 , 32p is the amorphous silicon layer of p mold, and 32i and 33i are the amorphous silicon layers

of i mold in drawing 3 . As shown in drawing 3 (b), when preparing i mold polycrystalline silicon layer which contains the grain of SiO2 inside in the part by the side of the optical incidence of i layer 3i, it is not necessary to prepare this layer in contact with p layer 3p.
[0032] Drawing 4 is structural drawing showing other examples of the photovoltaic cell of this invention. In this drawing, it is the transparent electrode which consists of SnO2 by which, as for 1, were-izing [SnO / the glass substrate] and, as for 2, the front face of 6000A of thickness was texture-ized. 3 consists of n-layer 3n of 1000A of thickness which consists of n mold polycrystalline silicon which is a solar-battery layer and is a dope layer by the side of i layer 3i and light transmission of 3000A of thickness which consists of i mold amorphous silicon of 100A of thickness which consists of p mold amorphous silicon carbide which is p layer 3p and a main optical generation-of-electrical-energy layer, and which contains the grain of SiO2 inside. 4 is a transparence conductive layer which consists of ITO, and 5 is a rear-face electrode which consists of Ag.
[0033] These forming methods are the same as the above-mentioned example. After forming n mold amorphous silicon which contains oxygen using a plasma-CVD method, it was made to crystallize by giving laser annealing, and n-layer 3n which consists of n mold polycrystalline silicon which contains the grain of SiO2 inside was formed.
[0034] If light carries out incidence to the photovoltaic cell of this example, i layers will not be absorbed by 3 but the light which penetrated this layer will be scattered about by two grains of SiO(s) in n mold polycrystalline silicon which constitutes n-layer 3n. As for the scattered light, in order to change an include angle and to reach the rear-face electrode 5, the dispersion component of light which it is reflected with the rear-face electrode 5, and carries out incidence to the solar-battery layer 3 again increases. For this reason, when the optical path length of the light within the solar-battery layer 3 increases, a deployment of light can be aimed at and the output current increases, photoelectric conversion efficiency improves.
[0035] The photoelectric conversion efficiency of the photovoltaic cell of this example which the particle size of two grains of SiO(s) was changed, and formed it is shown in a table 4. In addition, the photoelectric conversion efficiency of the photovoltaic cell of structure was 10.5% conventionally which was shown in drawing 8 .
[0036]
[A table 4]

粒径（ｎｍ）	光電変換効率（％）
5	１０．５
１０	１０．６
２０	１０．９
３０	１１．１
５０	１１．３
１００	１１．２

[0037] As shown in a table 4, when the particle size of two grains of SiO(s) was 5nm, the photoelectric conversion efficiency of the photovoltaic cell of this example did not have enough dispersion of light, and it was conventionally [10.5% and] the same as that of the photovoltaic cell of structure. [of it] However, particle size took for becoming large, photoelectric conversion efficiency improved, the photoelectric conversion efficiency in 10nm with a particle size higher than 10.6% and the former was acquired, and 11% or more of high photoelectric conversion efficiency was especially acquired by 30nm or more.
[0038] Moreover, although n mold polycrystalline silicon which contains the grain of SiO2 inside constituted n layer the 3n whole which is a dope layer by the side of light transmission from this example, a part of n layers may be

constituted from n mold polycrystalline silicon which contains the grain of SiO2 inside like the above-mentioned example, and the same effectiveness is acquired even if it prepares i mold polycrystalline silicon layer which contains the grain of SiO2 inside in the part by the side of the light transmission of i layers. These examples are shown in drawing 5 . This drawing is structural drawing of the photovoltaic cell which prepared 32n of n mold polycrystalline silicon layers which contain the grain of SiO2 inside in the part by the side of n layer 3n light transmission.

[0039] Drawing 6 is still more nearly another structural drawing of the photovoltaic cell of this invention. In this drawing (a), each constitutes n-layer p layer 3p and 3n from p mold polycrystalline silicon and n mold polycrystalline silicon which contain the grain of SiO2 inside. Moreover, this drawing (b) is structural drawing of the photovoltaic cell constituted from p mold polycrystalline silicon and i mold polycrystalline silicon by the side of p layer 3p and the light transmission of i layers with which each contains the grain of SiO2 for 31i inside in part. By making it such structures, since the scattering effect of the light by the side of optical incidence and a rear face can be attained simultaneously, much more deployment of incident light can be aimed at. In addition, it cannot be overemphasized that the same effectiveness is acquired even if constituted from i mold polycrystalline silicon and n mold polycrystalline silicon with which each contains the grain of SiO2 for the part by the side of the optical incidence of i layers and n layers inside instead of. [the structure of drawing 6 (b)]

[0040] Although amorphous silicon was used as an ingredient of a main optical generation-of-electrical-energy layer in the above example, it does not restrict to this and can apply also to the photovoltaic cell which used a-SiGe:H, crystal silicon, polycrystalline silicon, etc. as the main optical generation-of-electrical-energy layer.

[0041] Drawing 7 is structural drawing of the photovoltaic cell which used polycrystalline silicon as a main optical generation-of-electrical-energy layer. In this drawing, it is n mold polycrystalline silicon layer which contains two grains of SiO(s) of 2 micrometers of thickness from which 7 becomes a stainless steel substrate and 8 becomes a main generation-of-electrical-energy layer inside. The buffer layer to which 9 changes from i mold amorphous silicon of 50A of thickness, p layers to which 10 changes from p mold amorphous silicon of 200A of thickness, the transparent electrode with which 10 consists of ITO of 1000A of thickness, and 11 are collectors which consist of Ag.

[0042] By giving heat annealing at the temperature of 800 degrees C in a vacuum for 10 hours, solid phase growth was carried out and the polycrystalline silicon layer 8 which contains SiO2 inside was formed, after forming n mold amorphous silicon which contains oxygen on the same conditions as a table 1 using a plasma-CVD method. Like the case of laser annealing which mentioned above also in solid phase growth, although amorphous silicon turns into polycrystalline silicon, by the presentation near SiO2 or this, it distributes at random in polycrystalline silicon, and the oxygen contained in amorphous silicon in that case is segregated, and becomes granular.

[0043] Also in the case of this example, incident light is scattered about by two grains of SiO(s) in n mold polycrystalline silicon 8, and when the optical path length of light increases, its output current improves.

[0044] In addition, a silicon nitride, lead oxide, tin oxide, CdS(s) and ZnP(s), or such mixture can be used in addition to SiO2 stated in the above example as matter with an optical small refractive index.

[0045]

[Effect of the Invention] The photovoltaic cell of this invention equips a part of photovoltaic-cell layer with the polycrystal semi-conductor layer containing the grain of the matter with an optical small refractive index. Incident light is scattered about with the grain of the matter with the optical small refractive index in a polycrystal semi-conductor layer. For this reason, according to the location in which this layer was prepared, or the optical path length in the inside of a photovoltaic-cell layer increases and the dispersion component of the reflected light in a rear face increases, the effectiveness of these both occurs and a deployment of incident light can be aimed at.

[0046] As matter with said optical small refractive index, a silicon oxide, a silicon nitride, lead oxide, tin oxide, CdS(s) and ZnP(s), or such combination can be used.

[0047] Moreover, since 10nm or more of particle size of the grain of the matter with an optical small refractive index is preferably set to 30nm or more, incident light can be scattered about effectively.

[Translation done.]